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(54) Title: GRANULES FOR THE PRODUCTION OF A MOULDING WITH A CLASS A SURFACE, PROCESS FOR THE PRODUCTION OF GRANULES AND ITS USE

(57) Abstract

The present invention relates to granules for the production of mouldings with a class A surface comprising a thermoplastic polymer and fiber material with a length within a range from 1 to 25 mm, wherein the fibers are extending in the direction of the length of the granule having at most the length of that granule, containing fiber filaments with a diameter of 1-5 μm, characterized in that 920 to 1000 filaments per 1000 filaments are enveloped by the thermoplastic polymer matrix as measured in the cross section of the granules and the percentage of this envelopment for a single enveloped filament in contact with the thermoplastic polymer is in the range from 80 to 100. Further subjects of the invention are a process for preparing the granules, the use of the granules and mouldings made from the granules.

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GRANULES FOR THE PRODUCTION OF A MOULDING WITH A CLASS A SURFACE, PROCESS FOR THE PRODUCTION OF GRANULES AND ITS USE

The present invention relates to a new granule which contains fiber reinforced material for the production a moulding with a class A surface, especially for automotive parts. Further subjects of the invention are a moulding made from the granules according to the invention and a process for the production of the granules according to the invention.

Injection moulded long fiber reinforced thermoplastic compounds offer a good combination of mechanical properties, compared to short fiber reinforced compounds and unreinforced injection moulded polymer blends. These compounds have a high strength, a high modulus and high dimensional stability and can be used, especially for moulding automotive parts.

The interest in long fiber reinforced compounds for injection moulding has therefore increased as a result of improved manufacturing methods which yield materials that are stronger and more consistent in performance than the short fiber products. The designer's and processors for thermoplastic polymers also are becoming more aware that these reinforcements require only minimum modification of part and mould design and of injection moulding machinery.

Long fiber materials differ from short fiber materials both in the method of manufacture and in the resulting properties. Conventional extrusion compounding of chopped glass fibers and polymer matrix leads to a melt-mixed product, which when strand pelletized yields pellets which are about 3 mm long and contain random fibers of about 0.3 mm fiber length.

In contrast thereto long fiber materials are normally made by pultrusion processes, wherein a continuous fiber strand is enveloped with a melted resin matrix, forming a rod or a tape. Thereafter that the rod or the tape is pelletized to a granule with a length of, for example, 10 mm containing parallel fibers wherein the fibers have a length of about 10 mm as well. The above described pultrusion process allows one to achieve fiber lengths between 10 and 20 times greater than those in short fiber compounds. In the granule obtained with the pultrusion process the fibers are extending in the direction of the length of the granule having at most the length of that granule. The fibers and the granules obtained with the pultrusion process have a length within a range from 1 to 25 mm, containing fiber filaments with a diameter of 1-20 μm.

For the long fiber compounds, polymers like nylon, polyolefines, polycarbonates, polyester, polyurethanes can be used as the polymer matrix. The polymer matrix may contain usual additives like fillers, stabilizers and impact modifiers. Glass fiber is the dominant reinforcing medium, but carbon and aramid fibers are also used.

From the state of the art several long

fiber reinforced thermoplastic compounds are known.

US 5,019,450 describes a long fiber reinforced thermoplastic material containing at least 30% by volume of reinforcing filaments extending longitudinally of the structure which have been produced in a continuous process. The thermoplastic material has an exceptionally high stiffness which results from thorough wetting of the reinforcing filaments by molten polymer in the continuous process.

EP 0 680 813 A1 describes a fiber reinforced plastic moulding composition produced by coating fibers in a fluidised bed of dry plastic granules, heating the coated fibers to soften the plastic, cooling and granulating it. The coated fibers can be processed into mouldings.

EP 0 554 950 A1 describes the preparation of a moulding of long fiber reinforced thermoplastic material using composite granules obtained by cutting polymer powder impregnated fiber filaments coated with an outer sheath of same or other polymer. The granules have been obtained by impregnating an open bundle of continuous, parallel fibers with a thermoplastic polymer powder, forming a continuous filament from the impregnated fibers, coating the filament with a continuous outer sheath of a thermoplastic polymer the same as or different to the polymer of the powder and having a melting point that is the same or higher than that of the powder polymer, calendering at approximately the powder polymers softening temperature and cutting the calendered filaments into granules.

When using the long fiber reinforced

thermoplastic compounds for the preparation of mouldings, especially for automotive parts, it is disadvantageous that the long fiber reinforced compounds of the state of the art have a poor dispersion of some big fiber bundles (for example 1 to 10 bundles of 100 to 1000 filaments per square meter) as well as small filament aggregates (for example 1 to 5 aggregates of more than 10 to 20 filaments per square mm) in the polymer matrix in the mouldings, for example in a fender or a bonnet. These pour dispersed big bundles give rise to irregularities in the surface of the moulding. The aggregates also give rise to poor surface properties and after the painting of the mouldings the aggregates give rise to a lot of orange peel which results in a waviness of the surface of the moulding. By using the long fiber reinforced thermoplastic materials according to the state of the art it is not possible to produce mouldings, especially automotive parts, with a surface that, fulfils the class A specification set by the automobile industry.

Therefore, it is the technical object of the present invention to provide a new long fiber reinforced thermoplastic material which does not show the above disadvantages when injection moulded into a moulding, especially into automotive parts.

The technical problem is solved by a granule which is characterised in that 920 to 1000 filaments per 1000 filaments are enveloped by the thermoplastic polymer matrix as measured in the cross-section of the granules and the percentage of this envelopment for a single enveloped filament in contact

with the thermoplastic polymer is in the range from 80 to 100.

It is preferred that 950 to 1000, more preferably 990 to 1000 and most preferred 995 to 1000 filaments per 1000 filaments are enveloped. The percentage of the envelopment for the single enveloped filament in contact with the polymer matrix is preferably in the range of 90 to 100, more preferred 95 to 100. In a further preferred embodiment the concentration of the fiber in the granules is between 20 to 80% by weight, preferably 40 to 80% by weight. The thermoplastic polymer which is used for the granules is selected from the group comprising polyethylene, polypropylene, polyamide, polycarbonate, polyester, polyurethane, polyethylenterephthalate, polybuthyleneterephthalate, ABS, SAN, polystyrene, polyphenyleneoxide or mixtures thereof. Usual additives, like impact modifier, short randomly distributed glass fibers, fillers and stabilizers can also be used.

It is further preferred to use fibers which are selected from the group comprising carbon fibers, glass fibers and aramid fibers. In a preferred embodiment the granulate contains carbon fiber. This leads to an electrically conductivity of the mouldings so that the mouldings can be electrostatically coated even if the mouldings comprise only 1 to 3 wt-%, preferably 1.5 to 2.5 wt-% of the moulding, long carbon fibers.

The fibers used contain fiber filaments with a diameter of 1-5 μm, preferably from 1-3 μm. The

smaller the diameter of the fiber filaments is, the better are the surface properties of the mouldings prepared from the granules according to the invention.

In the case glass-fibers are used the percentage of glass-fibers is lower than 65 wt-%, preferably lower 63 wt-% related to the granules. Preferably glass-fibers are used having a sizing content below 0.5 wt-%, preferably 0.3 wt-%. The sizing is a coating which is applied to the filaments after the production of the filaments generally by the glass-fiber producer.

The granules are preferably made by using an apparatus, which is described in WO 87/00563 and in NL-1004796. First the separation of the filaments is effected by spreading the filaments preferably by means of an airknife. After that a polymer powder is applied to the separated filaments. This polymer powder is preferably suspended in one or more gas streams and is then applied to the seperated filaments. In a third step the polymer powder, which is applied on the filaments, is melted in an oven whereby the consolidation of the polymer and the filaments into a tape takes place. After that the tape is cooled down and cut into the granules. It is further important to control the tension of the fibers during the process. The tension of the filaments during separation and application of the powder is put down until the granules according to the invention are obtained.

After these process steps the percentage of envelopment of the single filament in contact with the fiber is in the range between 80 and 100 % measured in

the cross-section of the granulate for at least 920 to 1000 filaments out of 1000 filaments.

These granules are used for the production of automotive parts with a class A surface, especially exterior body panels like fenders, hoods, bonnets, panels, trunk lids and door panels. Therefore a further subject of the invention is a moulding with class A surface properties which is obtainable from the granules according to the invention by injection moulding. According to a preferred embodiment a film sprue is used for the injection moulding and injection is carried out in form of a cascade injection.

It is also possible to use mixtures of the granules according to the invention with other granules of the state of the art; for example granules containing short fibers or granules with an other polymer matrix. However, these granules must be compatible to the granules of the present invention. If in the granules according to the invention carbon fibers are used, these can be used optionally in combination with glass-fibers.

In the case that nylon 66, glass fiber and a mineral filler are used for the granules of the present invention, a further surprising effect occurs. The resulting moulded parts show high dimension stability. This is advantageous, because during the painting process, which is usually done by an electrophoresis process in car manufacturing, temperatures between 180° and 210°C are used. It was surprisingly found that the moulded parts sustain the conditions of this electrophoresis process with the

high temperatures very well. The painted mouldings showed an excellent class A surface without any dimensional change.

With the granules according to the state of the art it was not possible to prepare mouldings which have class A surface properties. The quality of the class A surface can be defined by the distinctness of image (D.O.I.) which is a determination of reflected light waves. This distinctness of image is determined as percentage of reflected light waves which are reflected from the surface of the moulded article measured in a certain angle of reflection. In the present invention mouldings containing the granules according to the invention have a very good value for D.O.I. when compared to the values of the D.O.I.'s for mouldings from the granules of the state of the art.

The mouldings made from the granules according to the invention can be used as a replacement material for automotive body panels made from metal. They show similar mechanical properties, but the mouldings made from the long fiber reinforced material show a significant lower specific gravity which means that by using these material instead of metallic body panels the automobile finally has a lower weight and therefore a decreased consumption of fuel.

In the following examples the invention will be described in more detail.

<u>Examples</u>

Long fiber reinforced thermoplastic

materials were produced by different methods and were compared with materials which are short fiber reinforced, unreinforced thermoplastic material and steel. From these thermoplastic materials mouldings were made and the surface properties of these mouldings were measured according to the distinctness of image (D.O.I.) in order to determine if the mouldings have a class A surface.

The following properties were measured:

1. Orange Peel - (Shortterm Waviness)

   Orange peel was measured after moulding and painting of the panel. The orange peel is related to a waviness of the surface of the panel of 1 to 1.5 mm. The sample surface is scanned by a point source laser by moving the laser over a distance of 10 cm. The light source illuminates the surface at 60° and the reflected light is measured at the same but opposite angle. When the light beam hits a peak or a valley of the surface a maximum signal is detected, on the slopes a minimum signal is registered. The higher the part of the reflected light is, the lower is the orange peel of the surface.

   For the measurement of Orange Peel a Byk wave scan apparatus of Byk Gardner, USA is used.

2. D.-Sight-Index

   The D.-Sight-Index was measured according to D.O.I. (distinctness of image) on the surface of

the moulded and painted panel. This measurement was executed in the wavelength range of the panel of 0.2 to 0.5 cm. The medium term waviness which was measured gives data about the roughness and the coating of the mouldings. The lower the number for the D.-Sight-Index, the better is the reflection of the light which was put on the surface of the moulding. The D.-Sight-Index is measured by a Diffracto® D-sight apparatus of Diffracto, USA.

3. Longterm Waviness (L.T.W.)
Long term waviness was also measured according to D.O.I. (distinctness of image). L.T.W. was measured at a wavelength of the panel between 1 and 20 cm.

The longterm waviness was measured by Diffracto® D-sight apparatus of Diffracto, USA.

The properties of panels of the following thermoplastic compositions were determined. The result are shown in Table 1.

a1: a dry blend of PA granules and granules of PA reinforced with powder-impregnated carbon fibers. The diameter of the carbon filaments was 5 μm

a2: a dry blend of PA granules and granules of PA reinforced with powder-impregnated glass fibers. The diameter of the glass filaments was 10 μm.

a3: a dry blend of PA granules and granules of PA

reinforced with powder-impregnated carbon fibers. The diameter of the carbon filaments was 7 µm.

a4: granules of PA reinforced with pultruded glass fibers, partly surrounded. The diameter of the glass filaments was 5 µm.

a5: granules of PA reinforced with wire coated glass fibers. The diameter of the glass filaments was 5 µm.

a6: granules of PP reinforced with wire coated comingled glass fibers and PP fibers. The diameter of the filaments was 10 µm.

a7: granules of PA and granules of a wire coated high sized glass fiber (4 to 8 wt.% sizing).

b: long glass fiber reinforced thermosets (polyesters)

c: unreinforced thermoplastic blends (PA/PPO/rubber or PC/PBT)

d: steel

Abbrevations:	PA	=	polyamide 6
	PP	=	polypropylene
	PBT	=	polybutyleneterephthalate
	PC	=	polycarbonate
	PPO	=	polyphenyleneoxide

All compositions except A1-A3 are compositions according to the state of art. Composition A1 is a composition according to the invention.

The compositions of A1-A7 contained about 15 wt.% fibers with a fiber length of 1-25 mm. The composition B contained about 25 wt.% glass fiber.

Preparation of granules A1-A3

The granules were made by using the apparatus, which is described in WO 87/00563 and in NL-1004796. First the separation of the filaments was effected by spreading the filaments preferably by means of an airknife. After that PA powder was applied to the separated filaments. This PA powder was suspended in one or more gas streams and was then directed to the separated filaments. In a third step the PA powder, which was applied to the filaments, was melted in an oven whereby the consolidation of the polymer and the filaments into a tape took place. After that the tape was cooled down and cut into the granules. After these process steps the percentage of envelopment of the single filament in contact with a fiber was in the range between 95 and 100 % measured in the cross-section of the granules. The tension of the filaments during separation and application of the powder was put down as low as possible to keep the process running until the granulate according to the invention was obtained.

Measurement of envelopment

The percentage of envelopment of the single filament in contact with the polymer in the cross-section of the granules was measured as follows: A granule was embedded in an epoxy-resin and the embedded grain was cut perpendicular to the direction of the glass-fibers. The cross-section of the reinforcing fibers perpendicular to the orientation direction of

the fibers was exposed to grinding and polishing for 1 minute using silicium carbide (SIC) wet papers of numbers 220, 500, 1000 and 2400 and additionally diamond slurries with a particle size of 6 μm, 1 μm were used for polishing for 1.5 minutes. The scanning electron microscope (SEM) image of the polished surface was photographed. The envelopment was determined from the SEM-photo manually. Determined was the percentage of envelopment of the filaments and the percentage of envelopment of the single filament.

From Table 1 can be seen that the granule a1 according to the invention shows results which are better than the results of steel (see d.) and also better than the results of other reinforced materials (see a2 to a7). Therefore with the granules according to the invention it is possible to produce mouldings with a class A surface with high and excellent quality, preferably for the automotive industry.

Table 1

Material	orange peel	D.-Sight-Index	L.T.W.	bundles (50-1000 filament/m^2)	bundles aggregates more than 1-10 per mm^2	class A surface	enveloped filaments (of 1000)	% of envelopment
a1.	2- 3	40- 70	50- 80	none	none	yes	997	95-100
a2.	5-6	70-100	50- 80	none	none	no	997	95-100
a3.	4-5	70- 90	50- 80	none	none	no	997	95-100
a4.	6-10	80-150	50- 80	5- 20	5-10	no	915	95-100
a5.	7-10	80-150	50- 80	10-100	8-15	no	0	0
a6.	8-11	80-150	50- 80	20- 50	7-20	no	0	0
a7.	7-10	80-150	50- 80	10- 30	5-10	no	0	0
b.	2- 3	20- 75	40- 60	10-100	-	yes	500	50-100
c.	2- 3	50- 80	130	none	none	yes	-	-
d.	2- 3	49	76	none	none	yes	-	-

CLAIMS

1. Granules for the production of a moulding with a class A surface comprising a thermoplastic polymer and fiber material with a length within a range from 1 to 25 mm, containing fiber filaments with a diameter of 1-5 μm, wherein the fibers are extending in the direction of the length of the granule having at most the length of that granule characterized in that 920 to 1000 filaments per 1000 filaments are enveloped by the thermoplastic polymer as measured in the cross-section of the granules and the percentage of this envelopment for a single enveloped filament in contact with the thermoplastic polymer is in the range from 80 to 100.

2. Granules according to claim 1, wherein the percentage of envelopment for the single enveloped filament is 90 to 100.

3. Granules according to claim 1, wherein the percentage of envelopment for the single enveloped filament is 95 to 100.

4. Granules according to anyone of claims 1 to 3, wherein 950 to 1000 filaments per 1000 filaments are enveloped.

5. Granules according to anyone of claims 1 to 3, wherein 990 to 1000 filaments per 1000 filaments are enveloped.

6. Granules according to anyone of claims 1 to 3, wherein 995 to 1000 filaments per 1000 filaments are enveloped.

7. Granules according to anyone of claims 1 to 6, wherein the thermoplastic polymer is selected from the group comprising polyethylene, polypropylene, polyamide, polycarbonate, polyester, polyurethane, polyethylenterephthalate, polybuthyleneterephthalate, polystyrene, ABS, SAN, polyphenyleneoxide, or mixtures thereof.

8. Granules according to anyone of claims 1 to 7, wherein the fibers are selected from the group comprising carbon fibers, glass fibers, aramid fibers.

9. Granules according to anyone of claims 1 to 8, wherein the fibers comprise carbon fibers.

10. Granules according to anyone of claims 1-8, wherein the diameter of the fiber filaments is 1-3 μm.

11. Process for the production of the granules according to anyone of claims 1 to 10, by the following steps:

- spreading the filaments of the fiber material
- applying polymer powder to the separated filaments
- melting the polymer
- consolidation of the molten polymer and the filaments into a tape
- cooling down the tape
- cutting the tape into the granules
- characterized in that the tension of the filaments during the process is put as down

as possible to keep the process running until the granules of claims 1 to 11 are obtained.

12. Use of the granules according to anyone of claims 1 to 10, for the production automotive parts with a class A surface.

13. Moulding with a class A surface, obtainable from the granules according to any one of claims 1 to 10 by injection moulding.

14. Moulding according to claim 13, wherein the moulding is an automotive part.

15. Moulding according to claim 13 or 14, wherein carbon fibers are used, optionally, in combination with glass-fibers.

16. Moulding according to anyone of claims 13 to 15, wherein the moulding contains 1 to 3 % by weight carbon fibers.

17. Mouldings according to anyone of claims 13 to 15, wherein the moulding contains 1.5 to 2.5 wt-% of carbon fibers.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29B9/14 B29B15/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y A	EP 0 386 266 A (ASAHI CHEMICAL IND) 12 September 1990 (1990-09-12) page 3, line 20 -page 4, line 16 page 5, line 1 -page 8, line 10 page 11, line 23 -page 12, line 18 page 46, line 1 -page 47, line 16; claims ---	9,10,12, 14-17 1-8,13
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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